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Influence of temperature on the selectivity of dissociation of CF_3I molecules by multiphoton vibrational and subsequent electronic excitation

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A report is given of theoretical and experimental studies of the influence of temperature on the selectivity of separating carbon isotopes by multiphoton vibrational and subsequent electronic excitation of CF_3I molecules. Carbon dioxide laser radiation was used for vibrational excitation and XeCl and XeF excimer lasers were used for dissociation. A selectivity of 108 was achieved at 223 °K.

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1. The development of methods of selective laser irradiation of materials has resulted in the recent development of efficient methods of laser isotope separation (see the reviews presented in Refs. 1 and 2). Multiphoton dissociation of molecules in a high-intensity infrared laser field has been widely used[3] and isotopes of many elements have been separated by this method. A substantial improvement to this method was achieved by dissociation in a two-frequency infrared field.[4] This method is efficient for separating isotopes of heavy elements since the functions of selective excitation and dissociation of the molecules are separate. In these two methods, dissociation of the molecules takes place within the ground electronic state.

There are also two methods of isotope separation involving dissociation of the molecules via an excited electronic state. The first method involves two-stage dissociation of molecules on exposure to infrared and ultraviolet sources.[5] In this case, the ultraviolet radiation causes dissociation of molecules preexcited by the infrared radiation. In the second approach, multiphoton vibrational excitation of the molecules is achieved below the dissociation limit, followed by excitation to an electronic state.[6,7]

Isotopically selective dissociation of CF_3I molecules by multiphoton vibrational excitation was first achieved in Ref. 8. The influence of temperature on the selectivity of multiphoton dissociation and the multiphoton absorption spectrum of CF_3I molecules were investigated in Refs. 9 and 10.

It was shown in our previous investigations[6,7] that the selectivity of isotope separation by multiphoton vibrational and subsequent electronic excitation of $^{12}CF_3I$ molecules is governed by the ratio of the ultraviolet absorption cross sections of excited and unexcited molecules and is limited by thermal population of high vibrational levels.

The ultraviolet absorption spectra of $^{12}CF_3I$ and $^{13}CF_3I$ molecules are almost the same. Thus, when the gas is irradiated only by an ultraviolet laser, molecules containing both ^{12}C and ^{13}C dissociate equally. Since under conditions of multiphoton vibrational and subsequent electronic excitation, dissociation is achieved only by the ultraviolet laser radiation, the selectivity of the isotope separation process is governed by the ultraviolet absorption cross sections of the vibrationally excited (for example, $^{12}CF_3I$) and unexcited molecules ($^{13}CF_3I$).

For the energy density of the infrared radiation used (0.2 J/cm^2), no appreciable broadening of the multiphoton absorption spectrum of the CF_3I molecules is found compared with the linear spectrum.[10] The selectivity of the infrared excitation [$R(14)$ line, 9.2 μ] may be determined from the known isotope shift (26.5 cm^{-1}). It is found that this selectivity is appreciably higher than the selectivity of excitation in the ultraviolet channel after the infrared pulse. Thus, the resultant selectivity depends mainly on the ratio of the ultraviolet absorption cross sections of the vibrationally excited (σ^{ir+uv}) and unexcited (σ^{uv}) molecules, as shown in Ref. 7. It is found that under identical excitation conditions in the infrared channel, the selectivity of the isotope separation process is governed by the wavelength of the dissociating ultraviolet radiation and is approximately equal to the experimentally measured value $\sigma^{ir+uv}/\sigma^{uv}$ for λ^{uv}_{XeCl} = 308 nm and 48 for λ^{uv}_{XeF} = 350 nm. The selectivity may be increased by reducing the gas temperature. The present paper reports a study of the influence of temperature on the selectivity of the isotope separation process.

2. In the experiments the molecules were vibrationally excited by TEA CO_2 laser radiation on the $R(14)$ line of the 9.2 μ lasing band. This frequency falls within the Q branch of the $^{12}CF_3I$ molecules. The laser radiation pulse consisted of an initial spike of 100 nsec base duration and a tail of 500 nsec duration. The tail contained not more than 20% of the energy. The energy density of the infrared radiation at the entrance to the illuminated cell was 0.2 J/cm^2. The preexcited molecules were dissociated by radiation from XeF (λ = 350 nm) and XeCl (λ = 308 nm) excimer lasers. This involved focusing the ultraviolet radiation in the cell coaxially with the CO_2 laser radiation but from the opposite direction. The

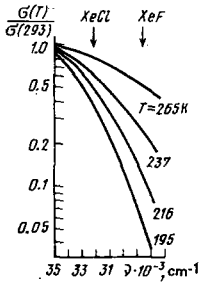

FIG. 1. Calculated dependences of the ratio $\sigma(T)\sigma(293)$ on the ultraviolet radiation frequency for different gas temperatures.

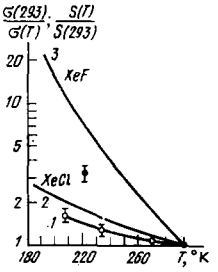

FIG. 2. Temperature dependences of the absorption cross section (2, 3) and selectivity (1): 1) λ_{XeCl}, $E_{ir}=0.2$ J/cm^2, $S(293)=2.0$; 2) α_{XeCl}; 3) α_{XeF}; •) λ_{XeF}, $E_{ir}=0.2$ J/cm^2, $S(293)=36$.

lasing frequencies of the excimer lasers were situated at the long-wavelength edge of the diffuse absorption band ($\nu_{max}=37\,500$ cm^{-1}). The pulse duration was 25 nsec and the energy reached 20 mJ. The active medium was formed by an NF_3:Xe:He = 1:3:600 mixture for the XeCl laser at a total pressure of 1.6 atm. The lasers were switched using TGI1-1000/25 thyratrons. The use of thyratrons made it easy to synchronize the infrared and ultraviolet lasers. The time delay between the CO_2 and excimer lasers was 100 ∓ 10 nsec. The CF_3I molecules were irradiated in a 14.7-cm long cell having a volume of 15 cm^3, cooled to −65 °C. The CF_3I pressure at room temperature was 0.2 Torr. The edges of the cell near the windows were at room temperature. The selectivity in the dissociation products was measured using an MI1309 mass spectrometer from the m/e = 119 and 120 peaks of the $C_2F_5^+$ fragment.

3. When the CF_3I molecules absorb radiation in the first electronic band, they dissociate with a quantum yield of ~1 to give CF_3 radicals and atomic iodine. Vibrational excitation of the CF_3I molecules sharply increases the ultraviolet absorption at the long-wavelength edge of the band and thus, when $^{12}CF_3I$ molecules are excited, they are preferentially dissociated by the ultraviolet radiation and the final C_2F_6 dissociation products are ^{12}C-enriched. On the other hand, when $^{13}CF_3I$ molecules are excited, the dissociation products are ^{13}C-enriched. The influence of the intensity of the exciting infrared field and of the wavelength of the dissociating radiation was investigated in detail in Ref. 7. The selectivity of the separation process, which is equal to the ratio of the isotope concentration in the dissociation products to the natural isotopic abundance, is governed by the ratio of the absorption cross sections of the excited σ^{ir+uv} and unexcited molecules σ^{uv}, $S = \sigma^{ir+uv}/\sigma^{uv}$. Evidently, as the temperature decreases, the value of σ^{uv} will decrease, increasing S. Figure 1 shows results of calculating the dependence of the absorption cross section $\sigma(T)$ relative to the absorption cross section at room temperature $\sigma(293)$ on the ultraviolet radiation frequency for different gas temperatures. The method of calculating the ultraviolet absorption spectrum was described in Ref. 7. As the temperature decreases, the population of the upper vibrational levels decreases and thus the absorption at the long-wavelength edge of the ultraviolet absorption band also decreases. The arrows in Fig. 1 show the lasing frequencies of the XeCl and XeF lasers. It can be seen that the largest decrease is found at the frequency of the XeF laser. For example, at 216 °K, the cross section decreases by a factor of 8.5.

As the temperature decreases, the infrared absorption spectrum also becomes narrower[10] and thus the radiation selectivity of vibrational excitation of the molecules increases. This is particularly important in the excitation of the $^{13}CF_3I$ molecules since, in this case, the infrared absorption by the $^{12}CF_3I$ molecules in hot bands decreases appreciably.

Thus, a decrease in the gas temperature should increase the selectivity of the multiphoton excitation process and enhance the selectivity of dissociation by ultraviolet radiation. It was shown in Ref. 11 that the rate constant for collisional vibrational–vibrational exchange k_{VV} for the CF_3I molecules is 2 μsec^{-1}·Torr^{-1} and in order to maximize the selectivity, it is necessary to decrease the gas pressure and the time delay between the infrared and ultraviolet pulses. In the experiments, the time delay τ_d was 100 nsec, which is appreciably shorter than $(k_{VV}p)^{-1}$.

Figure 2 (curve 1) shows the experimental temperature dependence of the relative change in the dissociation selectivity in the products $S(12/13)$ for dissociation by XeCl laser radiation and an infrared radiation density of 0.2 J/cm^2. At this infrared radiation density, no dissociation takes place due to the infrared radiation alone. At room temperature we find $S \approx 2.0$, which corresponds to an increase in the cross section for ultraviolet absorption by the CF_3I molecules immediately after the infrared exciting pulse.[7] Decreasing the temperature to 208 °K increases the selectivity by a factor of 1.6. Curve 2 in Fig. 2 shows the calculated dependence of the relative increase in the absorption cross section $\alpha = \sigma(293)/\sigma(T)$. If it is assumed that for a fixed infrared radiation density, a decrease in the gas temperature does not influence the absorption cross section of vibrationally excited molecules σ^{ir+uv}, curve 2 is the calculated dependence $S(T)/S(293)$. However, on comparing the calculations and experiment (curves 2 and 1), it is necessary to bear in mind that the edges of the cell were at room temperature and small warm sections of the cell may have reduced considerably the true selectivity. The contribution of the warm sections may be estimated from

$$\frac{S}{S(293)} = \frac{1+l_3/l_1}{1+(l_3/l_1)\,(S(293)/S(T))},$$

where $S(T)$ and $S(293)$ are the selectivities at a temp-

erature T and at room temperature, respectively; S is the measured selectivity; $l_2/l_1 = 3.1$ is the ratio of the lengths of the cold and warm sections of the cell. Thus, an increase in the ratio $S/S(293)$ by a factor of 1.6 implies that the selectivity $S(T)$ was doubled and thus was 4.0 at 208 °K. This value satisfactorily agrees with the calculated selectivity (curve 2).

For dissociation of vibrationally excited molecules by XeF laser radiation at room temperature and $E_{1r} = 0.2$ J/cm^2, we have $S(293) = 36$. Decreasing the temperature to 223 °K increases the selectivity to 108, i.e., trebles the selectivity. Curve 3 in Fig. 2 shows the calculated increase in selectivity as the temperature decreases.

It can be seen from this reasoning that decreasing the gas temperature is an effective method of increasing the the selectivity of dissociation by multiphoton vibrational and subsequent electronic excitation. This is useful for separating isotopes of heavy elements.

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[1]V. S. Letokhov, Usp. Fiz. Nauk **125**, 57 (1978) [Sov. Phys. Usp. **21**, 405 (1978)].
[2]V. S. Letokhov and C. B. Moore, Kvantovaya Elektron. (Moscow) **3**, 248 485 (1976) [Sov. J. Quantum Electron. **6**, 129, 259 (1976)].
[3]R. V. Ambartsumyan, V. S. Letokhov, E. A. Ryabov, and N. V. Chekalin, Pis'ma Zh. Eksp. Teor. Fiz. **20**, 597 (1974) [JETP Lett. **20**, 273 (1974)].
[4]R. V. Ambartsumyan, Yu. A. Gorokhov, G. N. Makarov, A. A. Puretskiĭ, and N. P. Furzikov, Kvantovaya Elektron. (Moscow) **3**, 1590 (1977) [Sov. J. Quantum Electron. **7**, 904 (1977)].
[5]R. V. Ambartsumyan, V. S. Letokhov, G. N. Makarov, and A. A. Puretskiĭ, Pis'ma Zh. Eksp. Teor. Fiz. **15**, 709 (1972); **17**, 91 (1973) [JETP Lett. **15**, 501 (1972); **17**, 63 (1973)].
[6]I. N. Knyazev, Yu. A. Kudryavtsev (Kudriavtsev), N. P. Kuz'mina, V. S. Letokhov, and A. A. Sarkisyan (Sarkisian), Appl. Phys. **17**, 427 (1978).
[7]I. N. Knyazev, Yu. A. Kudryavtsev, N. P. Kuz'mina, and V. S. Letokhov, Zh. Eksp. Teor. Fiz. **76**, 1281 (1979) [Sov. Phys. JETP **49**, 650 (1979)].
[8]S. Bittenson and P. L. Houston, J. Chem. Phys. **67**, 4819 (1977).
[9]V. N. Bagratashvili, V. S. Dolzhikov, V. S. Letokhov, and E. A. Ryabov, Pis'ma Zh. Tekh. Fiz. **4**, 1181 (1978) [Sov. Tech. Phys. Lett. **4**, 475 (1978)].
[10]S. S. Alimpiev, N. V. Karlov, A. M. Prokhorov, B. G. Sartakov, and É. M. Khokhlov, Kvantovaya Elektron. (Moscow) **6**, 2597 (1979) [Sov. J. Quantum Electron. **9**, 1536 (1979)].
[11]Yu. A. Kudryavtsev (Kudriavtsev) and V. S. Letokhov, Chem. Phys. **50**, 353 (1980).

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High-contrast nonlinear resonances in an He–Ne/I_2 ring laser

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High-contrast nonlinear resonances were obtained for the first time in an He–Ne/I_2 laser with a ring resonator. Nine nonlinear resonances were observed, having a maximum contrast ratio of ~0.5. It was found that the maximum contrast ratio of the resonances of a ring laser was almost independent of pressure.

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The present paper reports the first successful experiments to observe high-contrast nonlinear resonances in an He–Ne laser with an I_2^{129} absorbing medium, caused by coupling of opposite waves by means of back reflections.

The investigations were made using a ring laser with a quadrilateral resonantor having a 1 m perimeter. A 2.5-cm long cell containing I_2^{129} vapor was placed inside the resonator. Coupling between the opposite waves was achieved using an external return mirror. An additional Q factor difference was incorporated in the resonator, giving a stable fairly wide (~200 MHz) unidirectional lasing band in the absence of coupling. Coupling had the result that the intensity of the wave suppressed in the absence of coupling became nonzero.

Figure 1 shows an oscillogram of the dependence of the weak wave intensity on the frequency. In the unidirectional lasing zone, nine nonlinear resonances are clearly visible, corresponding to the m, n, a', c', d', t', f', g', and h' components of the hyperfine structure of I_2^{129} (for the notation of the components see Ref. 1). The maximum contrast ratio for the n component is

FIG. 1. Dependence of the weak wave intensity on the frequency in the one-wave lasing region.

